

Liquidus Equilibria in the System $\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{F}_2\text{O}_{-1}-\text{H}_2\text{O}$ to 100 MPa: I. Silicate–Fluoride Liquid Immiscibility in Anhydrous Systems

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Liquidus relations in the four-component system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{F}_2\text{O}_{-1}$ were studied at 0.1 and 100 MPa to define the location of fluoride–silicate liquid immiscibility and outline differentiation paths of fluorine-bearing silicic magmas. The fluoride–silicate liquid immiscibility spans the silica–albite–cryolite and silica–topaz–cryolite ternaries and the haplogranite–cryolite binary at greater than 960°C and 0.1–100 MPa. With increasing Al_2O_3 in the system and increasing aluminum/alkali cation ratio, the two-liquid gap contracts and migrates from the silica liquidus to the cryolite liquidus. The gap does not extend to subaluminous and peraluminous melt compositions. For all alkali feldspar–quartz-bearing systems, the miscibility gap remains located on the cryolite liquidus and is thus inaccessible to differentiating granitic and rhyolitic melts. In peralkaline systems, the magmatic differentiation is terminated at the albite–quartz–cryolite eutectic at ~770°C, 100 MPa, ~5 wt % F and cation $\text{Al}/\text{Na} = 0.75$. The addition of topaz, however, significantly lowers melting temperatures and allows strong fluorine enrichment in subaluminous compositions. At 100 MPa, the binary topaz–cryolite eutectic is located at 770°C, 39 wt % F, cation $\text{Al}/\text{Na} \sim 0.95$, and the ternary quartz–topaz–cryolite eutectic is found at 740°C, 32 wt % F, 30 wt % SiO_2 and cation $\text{Al}/\text{Na} \sim 0.95$. Such location of both eutectics enables fractionation paths of subaluminous quartz-saturated systems to produce fluorine-rich, SiO_2 -depleted and nepheline-normative residual liquids.

KEY WORDS: *silicate melt; granite; rhyolite; fluorine; liquid immiscibility*

INTRODUCTION

Fluorine is the most abundant and compatible volatile element in highly evolved granitic and rhyolitic magmas (Webster, 1990; London, 1997; Webster *et al.*, 1997; Thomas & Webster, 2000; Thomas *et al.*, 2005). The average fluorine concentrations in natural silicic suites increase from 0.11 wt % F in biotite and two-mica granites through 0.99 wt % F in topaz granites, rhyolites and ongonites (e.g. Kovalenko & Kovalenko, 1976; Štemprok, 1991; Dergachev, 1992) to ~3.9 wt % F in quartz topazites (e.g. Eadington & Nashar, 1978; Kortemeier & Burt, 1988; Zhu & Liu, 1990; Johnston & Chappell, 1992; Antipin *et al.*, 1999). This variability of fluorine abundances by nearly two orders of magnitude requires extreme levels of crystal–liquid fractionation (~99% solidified), if that process alone is responsible for the generation of the F-rich melts.

An alternative mechanism for generating high fluorine concentrations in residual magmatic liquids is provided by fluoride–silicate liquid–liquid immiscibility (e.g. Gramenitskiy & Shchekina, 1994; Veksler, 2004; Veksler *et al.*, 2005). Previous experimental studies, however, led to contradictory results concerning the presence and location of fluoride–silicate miscibility gaps (Table 1). These disagreements are found in simple systems, e.g. albite–NaF (Koster van Groos & Wyllie, 1968; Rutlin, 1998), and in multicomponent granitic systems (Kovalenko *et al.*, 1975; Glyuk & Trufanova, 1977; Kovalenko, 1977; Wyllie, 1979; Danckwerth, 1981; Webster *et al.*, 1987; Gramenitskiy & Shchekina, 1994; Xiong *et al.*, 2002).

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Table 1: Occurrence of the liquid–liquid immiscibility in fluoride–silicate systems

System	Pressure	Fluoride–silicate liquid immiscibility	
		Absent	Present
nepheline–NaF	1 atm		Kogarko & Krigman (1970, 1975) Bragina & Anfilogov (1980) Rutlin & Grande (1997) Færøyvik <i>et al.</i> (1999)
nepheline–Na ₃ AlF ₆	1 atm	Rutlin & Grande (1999) Siljan <i>et al.</i> (2001)	Kogarko & Krigman (1975) Pruttskov & Krivoruchko (1997)
albite–HF–H ₂ O	275 MPa	Wyllie & Tuttle (1961) Wyllie (1979)	
albite–NaF	1 atm	Koster van Groos & Wyllie (1968)	Kogarko & Krigman (1975) Bragina & Anfilogov (1980) Rutlin (1998)
albite–NaF–H ₂ O	100 MPa	Koster van Groos & Wyllie (1968)	
albite–Na ₃ AlF ₆	1 atm		Kogarko & Krigman (1975) Rutlin (1998)
Na ₂ SiO ₃ –NaF	1 atm	Willgallis (1969) Anfilogov <i>et al.</i> (1979)	
Na ₂ SiO ₃ –Na ₃ AlF ₆	1 atm		Kogarko & Krigman (1975)
Na ₂ Si ₂ O ₅ –NaF	1 atm	Willgallis (1969)	
Na ₂ Si ₂ O ₅ –Na ₃ AlF ₆	1 atm		Kogarko & Krigman (1975)
SiO ₂ –NaF	1 atm	Sedykh <i>et al.</i> (1998)	Anfilogov <i>et al.</i> (1979)
SiO ₂ –Na ₃ AlF ₆	1 atm		Kogarko & Krigman (1975)
SiO ₂ –Al ₂ O ₃ –Na ₃ AlF ₆	1 atm	Weill & Fyfe (1964)	
mullite–NaF	1 atm	Rutlin & Grande (1997, 1999)	
albite–SiO ₂ –NaF–Na ₃ AlF ₆	100 MPa		Koreneva & Zaiskiy (2001)
granite–NaF–H ₂ O	100 MPa		Anfilogov <i>et al.</i> (1973) Glyuk & Trufanova (1977)
granite–Na ₃ AlF ₆ –H ₂ O	100 MPa		Gramenitskiy & Shchekina (1994, 2001)
granite–NaF + AlF ₃ –H ₂ O	100 MPa	Manning (1981, 1982)	
	50–500 MPa	Webster (1990)	
granite–KF–H ₂ O	100 MPa		Glyuk & Anfilogov (1973 <i>b</i> , 1973 <i>c</i>) Glyuk & Trufanova (1977)
granite–HF–H ₂ O	100 MPa	Xiong <i>et al.</i> (1998, 1999)	Glyuk & Anfilogov (1973 <i>a</i>) Glyuk & Trufanova (1977) Kovalenko (1977)
	275 MPa	Wyllie & Tuttle (1961)	
	1 GPa	Danckwerth (1981)	
topaz granite (rhyolite)–HF–H ₂ O	50–100 MPa	Kovalenko <i>et al.</i> (1975)	
topaz granite–H ₂ O	100 MPa	Weidner & Martin (1987)	
	150 MPa	Xiong <i>et al.</i> (2002)	
	100–300 MPa	Pichavant <i>et al.</i> (1987)	
F-rich vitrophyre–H ₂ O	50–200 MPa	Webster <i>et al.</i> (1987)	

Additional studies of cryolite-based systems with metallurgical applications have been listed by Dolejš & Baker (2005).

These controversies are likely to result from: (1) misinterpretation of round fluoride crystals as immiscible globules (Gramenitskiy & Shchekina, 1994; Koreneva & Zarauskiy, 2001); (2) misinterpretation of stable or quench fluid inclusions with high solute content as immiscible liquids (microliquation; e.g. Anfilogov *et al.*, 1973; Gluyk & Anfilogov, 1973*a*, 1973*b*); (3) use of variable fluid or melt proportions during experiments, which causes significant departures from initial rock (melt) composition as a result of the fluid–melt partitioning; (4) mass loss and shift in melt composition as a result of fluoride vaporization in 1 atm experiments (Kogarko & Krigman, 1975; Siljan, 1990); (5) inappropriate choice of fluoride additives. The use of HF, alkali fluorides, NaF + AlF₃ mixtures or fluoride minerals produces very distinct compositional effects and such silicate–fluoride sections diverge from liquid lines of descent or intersect the Alkemade compatibilities; that is, they may penetrate potential thermal barriers.

Figure 1 illustrates mineral compatibilities between aluminosilicates and fluorides in the system (Na₂O + K₂O)–Al₂O₃–SiO₂–F₂O_{–1} at 700°C and 100 MPa (Dolejš & Baker, 2004). Increasing the chemical potential of F₂O_{–1} is equivalent to adding fluorine in the form of HF, which does not affect the major-oxide composition of the system. The phase diagram intersects numerous low- and high-fluorination assemblages (Anovitz *et al.*, 1987; Dolejš & Baker, 2004). However, only the low-fluorination assemblages are stable with alkali feldspar and therefore accessible to natural granitic magmas. Fluorination by adding alkali fluorides (NaF, KF) intersects the quartz–cryolite (elpasolite) tie-line where alkali feldspar becomes unstable and the resulting strongly peralkaline compositions are not representative of natural magmas. Addition of NaF and AlF₃ mixtures to balance the alumina–alkali ratio causes departure towards SiO₂-poor (feldspathoidal) compositions and promotes the metastable absence of topaz. Thus, understanding chemical and mineral compatibilities is essential in experimental design and to closely approach the differentiation paths of silicic magmas.

In this study, we present liquidus equilibria in several subsystems of the four-component space Na₂O–Al₂O₃–SiO₂–F₂O_{–1} to locate the fluoride–silicate miscibility gap and its relation to the liquid lines of descent of granitic and rhyolitic magmas. First, we calculate stabilities of fluoride phases in the haplogranite system during progressive fluorination and predict saturating solid phases. Second, we experimentally investigate several binary, ternary and quaternary systems that correspond to stable silicate–fluoride assemblages. The silica–cryolite binary is expected to intersect the field of fluoride–silicate liquid immiscibility and we trace its extension into

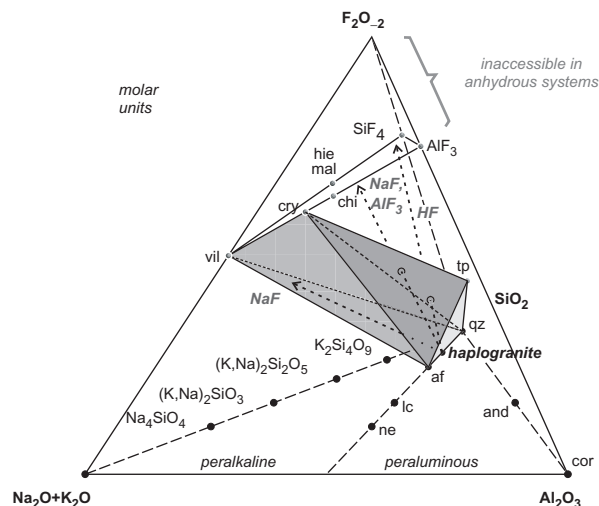


Fig. 1. Quaternary composition space (Na₂O + K₂O)–Al₂O₃–SiO₂–F₂O_{–1} with location of rock-forming minerals, topaz and fluoride phases. The edges of gray tetrahedra connect fluorine-bearing phases coexisting with quartz and alkali feldspar at 700°C and 100 MPa (Dolejš & Baker, 2004). The haplogranite composition corresponds to the Qz–Or–Ab minimum at 1 kbar and H₂O saturation (Tuttle & Bowen, 1958). Dashed trends originating at the haplogranite composition indicate compositional shifts by adding NaF, NaF + AlF₃ and HF; the latter two intersect additional compatibility tetrahedra that may not be accessible to natural differentiation paths owing to the separations of tetrahedra by peritectic transitions or thermal barriers.

the albite–quartz–cryolite and quartz–topaz–cryolite ternaries. The quartz–topaz–cryolite assemblage represents the products of albite fluorination, and this ternary system will be tested for peritectic relationships. We have performed experiments at 1 atm and at 100 MPa because this pressure range represents the typical emplacement levels of topaz granites, subvolcanic ongonite dykes and topaz rhyolites (Christiansen *et al.*, 1986; Štemprok, 1991; Cuney *et al.*, 1992; Price *et al.*, 1992; Thomas & Klemm, 1997). In the second part of this study (Dolejš & Baker, 2007), we report results on the hydrous albite–quartz and haplogranite systems with topaz and cryolite, which illustrate differentiation paths of silicic magmas and provide information on the maximum solubilities of fluorine and H₂O. These experimental results provide a complete framework for phase equilibria in fluorine-bearing, Li-, Ca- and Fe-poor, silicic magmas that range from peralkaline to peraluminous compositions.

COMPOSITION SPACE AND PHASE COMPATIBILITIES

Felsic igneous rocks span the composition space Na₂O–K₂O–Al₂O₃–SiO₂ (+H₂O). Individual phases are

defined in Table 2. Fluorine is a fifth component and it is a monovalent anion in all solid, liquid and gaseous phases in this study. The corresponding chemical component must contain fluorine in the same valence state; suitable options are NaF, KF, AlF_3 , SiF_4 or F_2O_{-1} . Although use of the fluorine molecule, F_2 , may appear to be obvious, we shall demonstrate below that because its valence state (0) differs from that of fluorine in all geological phases (-1) it is a poor choice.

To illustrate various choices of components, we will consider three-phase equilibrium of quartz, andalusite and fluortopaz. This assemblage contains three chemical components and one possible set is Al_2O_3 , SiO_2 and SiF_4 . The equilibrium between the three phases is given by equation 1 in Table 3. Another valid set of chemical components is Al_2O_3 , SiO_2 and F_2O_{-1} , and in this case the equilibrium has a simpler form (equation 2, Table 3). This is because the Al:Si ratio in andalusite and fluortopaz is the same and F_2O_{-1} does not contain any cation. The use of F_2O_{-1} does not change the proportions of cations in the multicomponent systems and it leads to simpler equilibrium expressions. A third choice of chemical components for our system is to split the exchange operator F_2O_{-1} into two components, F_2 and O_2 . This may appear intuitive but it has disadvantages because it introduces an additional component and the quartz–andalusite–fluortopaz assemblage must be described by Al_2O_3 , SiO_2 , F_2 and O_2 (see equation 3, Table 3). Furthermore, the choice of F_2 as a component requires that the oxygen fugacity of the system be defined. Oxygen is only needed to balance the difference between F^- (in topaz) and F^0 (in the F_2 component) but it is not required for any mineral–mineral equilibrium. When a component with a fluoride anion such as SiF_4 or F_2O_{-1} is chosen the oxygen-fugacity constraint is eliminated. We prefer to use the F_2O_{-1} component (Burt, 1972, 1975; Burt & London, 1982), an exchange operator that corresponds to a replacement of one oxygen by two fluorine anions, because this component maintains charge balance and keeps ratios of all cations constant (Dolejš & Baker, 2004). The use of the exchange operator F_2O_{-1} is thermodynamically valid (Burt, 1972, 1975), results in a correct number of system components and does not produce any loss of generality.

The anion exchange operator, F_2O_{-1} , is used here to describe fluorination of oxides and silicates into fluorides or topaz (Table 3). In H_2O -bearing systems, increases in F_2O_{-1} can also be visualized as addition of HF (see equation 4, Table 3). Also, HF and F_2O_{-1} projection points are identical (Fig. 1). In anhydrous systems, F_2O_{-1} is a hypothetical composition and this apex is physically inaccessible (upper part of Fig. 1).

To portray equilibria in the five-component system Na_2O – K_2O – Al_2O_3 – SiO_2 – F_2O_{-1} we use the reduced tetrahedron ($\text{Na}_2\text{O} + \text{K}_2\text{O}$)– Al_2O_3 – SiO_2 – F_2O_{-1}

Table 2: List of phases, their abbreviations and compositions

Abbreviation	Phase	Chemical formula
ab	albite	$\text{NaAlSi}_3\text{O}_8$
af	alkali feldspar	$(\text{Na},\text{K})\text{AlSi}_3\text{O}_8$
AF	aluminum fluoride	AlF_3
and	andalusite	Al_2SiO_5
chi	chiolite	$\text{Na}_5\text{Al}_3\text{F}_{14}$
cor	corundum	Al_2O_3
cry	cryolite	Na_3AlF_6
fsp	alkali feldspar	$(\text{Na},\text{K})\text{AlSi}_3\text{O}_8$
hie	hieratite	K_2SiF_6
KAF	potassium aluminum fluoride	KAlF_4
kf	potassium feldspar	KAlSi_3O_8
L	liquid (melt)	
L_{fl}	fluoride melt	
L_{sil}	silicate melt	
lc	leucite	KAlSi_2O_6
mal	malladrite	Na_2SiF_6
mus	muscovite	$\text{KAl}_2[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$
ne	nepheline	NaAlSiO_4
qz	quartz	SiO_2
SiO_2	silica polymorph	SiO_2
tp	fluortopaz	$\text{Al}_2\text{SiO}_4\text{F}_2$
trd	tridymite	SiO_2
V	aqueous vapor	
vil	villiaumite	NaF
X	solid phase(s)	

Phase proportions associated with abbreviations (e.g. $\text{Cry}_{53}\text{Tp}_{47}$) are given in weight per cent. For divariant fields and trivariant volumes, we use standard labeling (e.g. $\text{L} + \text{tp}$). For univariant curves and invariant points, we use the notation of Greig *et al.* (1955), e.g. $\text{L}(\text{cry})$ indicates a univariant boundary between L and $\text{L} + \text{cry}$ fields. Similarly, $\text{L}_{\text{sil}} + \text{qz}$ ($\text{L}_{\text{fl}} + \text{cry}$) is an invariant point at the intersection of four fields: $\text{L}_{\text{sil}} + \text{qz}$, $\text{L}_{\text{sil}} + \text{qz} + \text{cry}$, $\text{L}_{\text{sil}} + \text{L}_{\text{fl}} + \text{qz}$ and $\text{L}_{\text{sil}} + \text{L}_{\text{fl}} + \text{qz} + \text{cry}$.

(Fig. 1). This pseudoquaternary system contains important rock-forming minerals (quartz, micas, feldspars, feldspathoids) as well as fluorine-bearing phases (topaz, villaumite, cryolite, chiolite, malladrite, etc.) and the composition space includes both peralkaline and peraluminous compositions. Projection points of fluorides are obtained by combining oxides with F_2O_{-1} in stoichiometric proportions (equations 4–9, Table 3). Various trends of fluorination (i.e. addition of HF, NaF, AlF_3 , etc.) are easily illustrated with respect to phase locations and compatibilities. A complete analysis of fluorination reactions, silicate–fluoride equilibria and mineral compatibilities has been presented by Dolejš & Baker (2004).

Table 3: Summary of chemical equilibria

Number	Equilibrium
1	2 and + SiF ₄ = 2 tp + qz
2	and + F ₂ O ₋₁ = tp
3	and + F ₂ = tp + ½ O ₂
4	H ₂ O + F ₂ O ₋₁ = 2 HF
5	Na ₂ O + F ₂ O ₋₁ = 2 NaF
6	Na ₂ O + F ₂ O ₋₁ = (NaF) ₂
7	2 Al ₂ O ₃ + 6 F ₂ O ₋₁ = 4 AlF ₃
8	Na ₂ O + Al ₂ O ₃ + 4 F ₂ O ₋₁ = 2 NaAlF ₄
9	SiO ₂ + 2 F ₂ O ₋₁ = SiF ₄
10	3 ab + 4 F ₂ O ₋₁ = cry + tp + 8 qz
11	mus + qz = kf + and + H ₂ O
12	mus + qz + F ₂ O ₋₁ = kf + top + H ₂ O
13	5 cry + 2 tp + 4 F ₂ O ₋₁ = 3 chi + 2 qz
14	kf + 2 F ₂ O ₋₁ = KAlF ₄ + 3 qz
15	tp + 2 F ₂ O ₋₁ = 2 AlF ₃ + qz
16	2 KAlF ₄ + qz + 2 F ₂ O ₋₁ = hie + 2 AlF ₃
17	2 chi + 5 qz + 10 F ₂ O ₋₁ = 5 mal + 6 AlF ₃
18	SiO ₂ = qz
19	Na ₂ O + Al ₂ O ₃ + 6 SiO ₂ = 2 ab
20	Na ₂ O + Al ₂ O ₃ + F ₂ O ₋₁ = cry
21	Al ₂ O ₃ + SiO ₂ + F ₂ O ₋₁ = tp
22	Na ₃ AlF ₆ + 4 SiO ₂ = SiF ₄ + NaAlSi ₃ O ₈ + 2 NaF
23	2 Na ₃ AlF ₆ + 13 SiO ₂ = 3 SiF ₄ + 2 NaAlSi ₃ O ₈ + 2 Na ₂ Si ₂ O ₅

The formation of fluorine-bearing minerals in granitic systems corresponds to progressive fluorination of rock-forming silicates, defined by increasing chemical potential of F₂O₋₁. With increasing $\mu(\text{F}_2\text{O}_{-1})$, rock-forming minerals are converted to topaz, cryolite, chiolite and other fluoride minerals or gases (Fig. 2; equations 2 and 10–17, Table 3). In granitic rocks, fluorine concentrations are buffered by quartz, feldspar, topaz and cryolite (equation 10, Table 3) which corresponds to the first fluorination equilibrium in Fig. 2. The formation of the ‘high-fluorination’ phases (e.g. chiolite, malladrite) occurs after complete breakdown of feldspars. During magmatic crystallization, the accessibility of these ‘high-fluorination’ assemblages depends upon whether boundaries between specific phase assemblages (Fig. 2) become thermal barriers or peritectic transitions. If they form thermal barriers, magmatic differentiation will be restricted to relatively low fluorine contents, buffered by topaz and/or cryolite in the presence of quartz and feldspar (compare topaz granites, cryolite granites), whereas if they become peritectic transitions, residual magmas will achieve very high fluorine contents and become feldspar-absent (compare quartz topazites).

To know which topology is relevant, we must determine liquidus relations in degenerate sections (e.g. the cryolite–topaz–quartz ternary, Fig. 1) and test for the presence of pseudoternary phases (e.g. albite).

FLUORIDE VAPORIZATION

During experimental studies at high concentrations of fluorine, vapor pressures of aluminofluorides and silicofluorides increase, these species variably vaporize, and the loss of elements from high-temperature fluorosilicate liquids causes departures from the initial bulk composition (e.g. Snow & Welch, 1972; Siljan, 1990; Pruttskov & Krivoruchko, 1997). To approach this problem, we have evaluated vapor pressures in equilibrium with relevant solid and liquid phases. We use several examples in the system albite–quartz–cryolite–topaz to illustrate the necessary thermodynamic approach to vapor–solid and vapor–liquid fluorosilicate systems.

In each compatibility subtetrahedron (Fig. 1), the four coexisting phases at the pressure and temperature of interest uniquely define chemical potentials of four independent components. For example, the coexistence of albite, quartz, cryolite and topaz determines the chemical potentials of Na₂O, Al₂O₃, SiO₂ and F₂O₋₁, and their values are found by solving sets of linear equations containing the Gibbs free energies of the stable phases at the pressure and temperature of interest (equations 18–21, Table 3; Korzhinskii, 1959; Connolly, 1990; Dolejš & Baker, 2004). The chemical potentials of the independent components define the chemical potential (or fugacity) of any gaseous species of interest (equations 5–9, Table 3). The calculated fugacities of the most abundant fluoride species are plotted in Fig. 3. Over the temperature range of 600–1200°C, the abundance of individual fluoride compounds varies as follows: SiF₄ > NaAlF₄ > AlF₃ > NaF > (NaF)₂. Individual fugacities (vapor pressures) differ by several orders of magnitude and SiF₄ closely defines the total vapor pressure. The gas fugacities increase with increasing temperature. At low temperatures, the total vapor pressure is less than 1 atm and gaseous fluorides will constitute only a small fraction of the space in the capsule during the experiments. At high temperatures, the experimental design requires confining pressure. Our calculations demonstrate that an applied pressure of 100 MPa in our experimental procedure completely eliminates problems with fluoride vaporization (Fig. 4).

In contrast to stoichiometric solid phases, the fluorosilicate melt composition is not constant and may continuously change during fluoride vaporization. We will illustrate this for melts along the silica–cryolite binary, which were studied previously (Weill & Fyfe, 1964; Kogarko & Krigman, 1975). Because SiF₄ is the

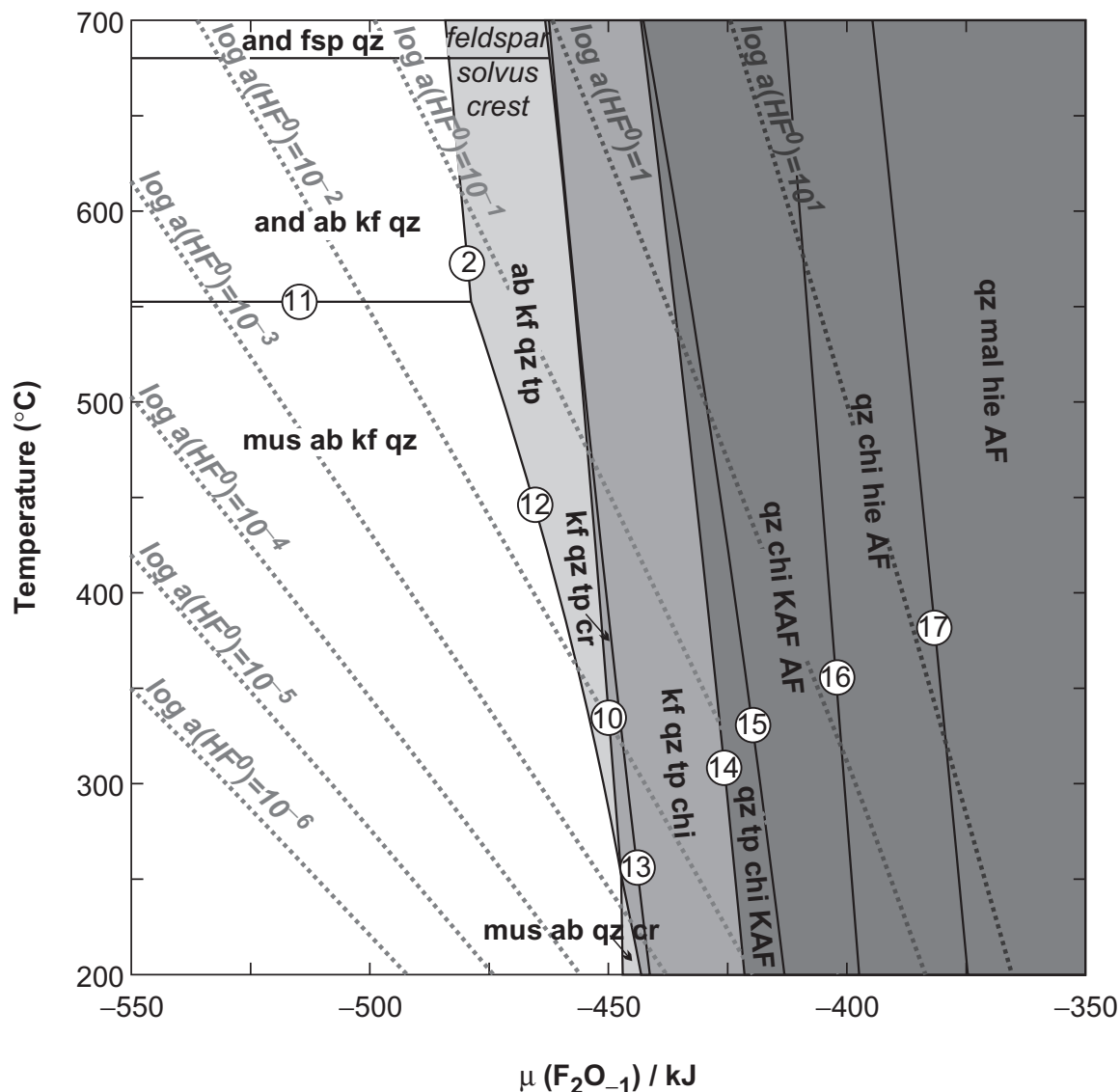


Fig. 2. Temperature– $\mu(\text{F}_2\text{O}_{-1})$ pseudo-section in the system $\text{qz-kf-ab-Al}_2\text{O}_3\text{-F}_2\text{O}_{-1}$ at 100 MPa and quartz and H_2O saturation. Bulk composition: $\text{Ab}_{60}\text{Or}_{40}$ + quartz and H_2O saturation, $\text{A/NK} = 1.2$. Thermodynamic data: Holland & Powell (1998) and Dolejš & Baker (2004); solid-solution models: topaz—Barton (1982); alkali-feldspar—Fuhrman & Lindsley (1988) and Wen & Nekvasil (1994). Isopleths of $a(\text{HF}^0)$ are calculated by the Helgeson–Kirkham–Flowers model (Shock *et al.*, 1989; Johnson *et al.*, 1992). Gray shading indicates stability of one, two or three fluorine-bearing phases, respectively. Labels of phase boundaries refer to equilibria in Table 3.

predominant gaseous species (Kogarko *et al.*, 1968; Snow & Welch, 1972; Siljan, 1990; Dolejš & Baker, 2004; Fig. 3), the melt composition deviates from the quartz–cryolite binary system to the ternary space where the third component is SiF_4 . The removal of SiF_4 from the $\text{SiO}_2\text{-Na}_3\text{AlF}_6$ binary shifts the melt composition within the $\text{SiO}_2\text{-Na}_3\text{AlF}_6\text{-SiF}_4$ plane away from the SiF_4 coordinate. That is, the melt composition leaves the $\text{SiO}_2\text{-Na}_3\text{AlF}_6$ tie-line in the $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-F}_2\text{O}_{-1}$ tetrahedron and enters one of the quaternary compatibility tetrahedra. By using the thermodynamic databases of Holland & Powell (1998)

and Dolejš & Baker (2004), the devolatilization equilibria are expressed by equation 22 (at $<896^\circ\text{C}$ and 1 atm) or equation 23 (at $>896^\circ\text{C}$ and 1 atm), respectively, in Table 3.

The quaternary assemblage is temperature-dependent, and these solid phases represent the solidus assemblage after crystallization of the degassed melt. These phases were observed in experimental run products (e.g. Snow & Welch, 1972; Pruttskov *et al.*, 1989) thus confirming the selective loss of fluorides to the vapor phase. To calculate fugacities of all fluoride species, the melt thermodynamics

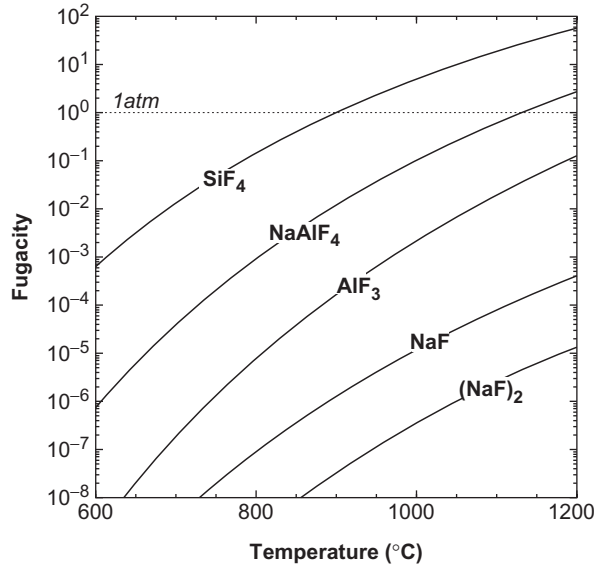


Fig. 3. Variations of fluoride fugacities with temperature, buffered by the quartz/tridymite–albite–topaz–cryolite assemblage (1 atm standard state); this four-phase assemblage represents a metastable buffer at high temperatures as a result of melting. The fugacity of SiF_4 was calculated by the compensated Redlich–Kwong equation in the corresponding state formulation (Holland & Powell, 1991); other gases are considered ideal. Thermodynamic data sources: Chase (1998); Devyatikh *et al.* (1999).

must be described by a non-ideal quaternary mixing model. We have calibrated a simple model for the $\text{NaAlSi}_3\text{O}_8$ – SiO_2 – $\text{Na}_2\text{Si}_2\text{O}_5$ – Na_3AlF_6 melt, by expanding the formulation of Holland & Powell (2001) and including experimental data in $\text{Na}_2\text{Si}_2\text{O}_5$ - and Na_3AlF_6 -bearing subsystems (Morey & Bowen, 1924; Kracek, 1930; Rutlin, 1998). The binary, asymmetric Margules parameters have the following values in the eight-anion formulation (Burnham, 1997; Holland & Powell, 2001): $W_{\text{Si}_4\text{O}_8-\text{NaAlSi}_3\text{O}_8} = W_{\text{NaAlSi}_3\text{O}_8-\text{Si}_4\text{O}_8} = 12 \text{ kJ}$, $W_{\text{Si}_4\text{O}_8-\text{Na}_3\text{AlF}_6} = W_{\text{Na}_3\text{AlF}_6-\text{Si}_4\text{O}_8} = 3 \text{ kJ}$, $W_{\text{Si}_4\text{O}_8-\text{Na}_2\text{Si}_2\text{O}_5} = 20 \text{ kJ}$, $W_{\text{Na}_2\text{Si}_2\text{O}_5-\text{Si}_4\text{O}_8} = 85 \text{ kJ}$, $W_{\text{NaAlSi}_3\text{O}_8-\text{Na}_2\text{Si}_2\text{O}_5} = 30 \text{ kJ}$, $W_{\text{Na}_2\text{Si}_2\text{O}_5-\text{NaAlSi}_3\text{O}_8} = -33 \text{ kJ}$; all remaining interaction terms are zero. At the temperature and pressure of interest, the degree of SiF_4 depletion in the melt is expressed by the extent of the devolatilization reaction (equation 22 or 23, Table 3), and the resulting melt composition is recast into four components (Si_4O_8 , $\text{NaAlSi}_3\text{O}_8$, $\text{Na}_2\text{Si}_2\text{O}_5$ and Na_3AlF_6) whose activities are now defined by the non-ideal mixing model. Chemical potentials of the four melt components uniquely define the chemical potentials of the system components (Na_2O , Al_2O_3 , SiO_2 , F_2O_{-1}) by linear-algebraic manipulation, and the fugacity of any fluoride gaseous species, coexisting with the fluorosilicate melt, is determined as above (equations 5–9, Table 3). We have

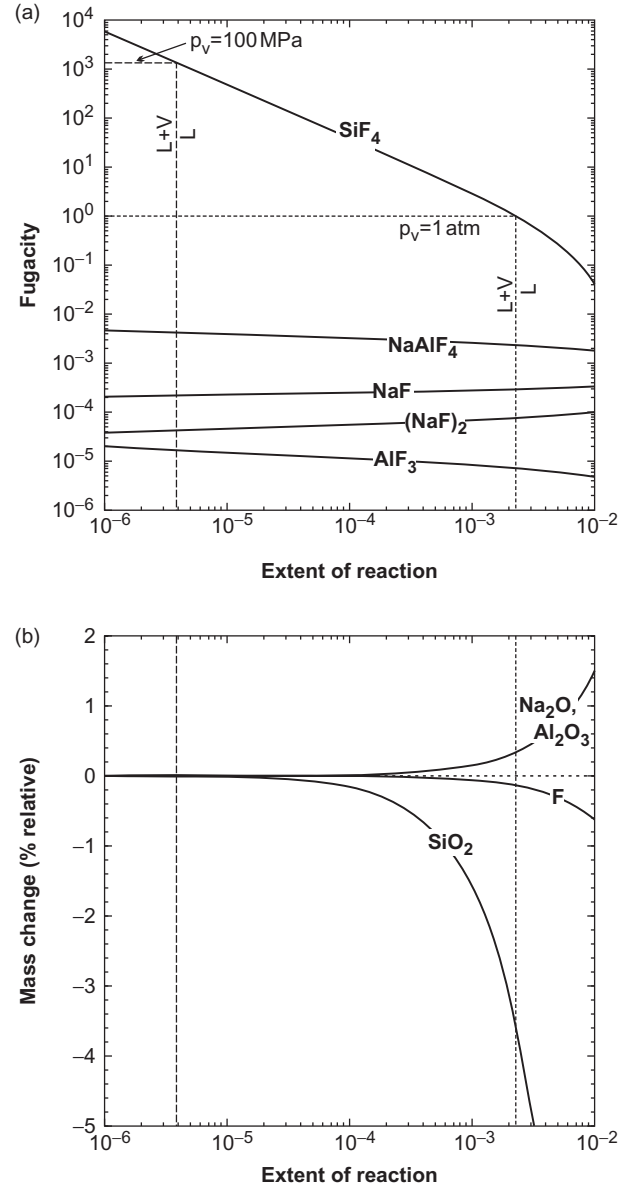


Fig. 4. Variations of fluoride fugacities in the vapor phase coexisting with a fluorosilicate melt at 1050°C and 1 atm. The melt composition is 95 wt % Na_3AlF_6 + 5 wt % SiO_2 and corresponds to the cryolite–tridymite eutectic. (a) Changes in vapor speciation controlled by the extent of the reaction $2 \text{ Na}_3\text{AlF}_6 + 13 \text{ SiO}_2 = 3 \text{ SiF}_4 + 2 \text{ NaAlSi}_3\text{O}_8 + 2 \text{ Na}_2\text{Si}_2\text{O}_5$ (equation 23, Table 3). Vertical dashed lines indicate the position of the L (V) boundary with respect to the total pressure. The extent of reaction and fluoride vaporization from the melt are greater at low pressures; (b) relative changes in the melt composition as a result of fluoride vaporization. Thermodynamic data sources: Holland & Powell (1991); Chase (1998); Devyatikh *et al.* (1999). The fluorosilicate melt is treated as a quaternary non-ideal asymmetric solution (see text for details).

portrayed the vapor pressures of gaseous species and compositional departures for various extents of devolatilization of the cryolite–silica eutectic melt (95 wt % Na_3AlF_6 and 5 wt % SiO_2) at 1050°C in Fig. 4.

Total vapor pressure at 1050°C ranges over several orders of magnitude and SiF_4 remains the predominant gaseous species. Both the total vapor pressure and the SiF_4 fugacity decrease with increasing extent of devolatilization (equation 23, Table 3) whereas fugacities of NaAlF_4 , NaF , $(\text{NaF})_2$ and AlF_3 change only insignificantly (Fig. 4a). The chemical potentials of system components (Na_2O , Al_2O_3 , SiO_2 , F_2O_{-1}) vary only negligibly over the small extent of the devolatilization equilibrium, $x = 10^{-6}$ to 10^{-2} (Fig. 4a). This means the fugacities of alkali fluoride and aluminofluoride species are relatively insensitive to x . In contrast, SiF_4 occurs in the devolatilization equilibrium (equation 23, Table 3) and is subject to the law of mass action, which includes other liquid species. As SiO_2 and Na_3AlF_6 react to produce SiF_4 , the mole fractions (and activities) of $\text{NaAlSi}_3\text{O}_8$ and $\text{Na}_2\text{Si}_2\text{O}_5$ increase in the melt but are initially very small numbers. As the equilibrium constant for equation 23 (Table 3), $K = f(\text{SiF}_4)^3 \cdot a(\text{NaAlSi}_3\text{O}_8)^2 \cdot a(\text{Na}_2\text{Si}_2\text{O}_5)^2 / [a(\text{Na}_3\text{AlF}_6)^2 \cdot a(\text{SiO}_2)^{13}]$, is a function of pressure and temperature only, small activities of $\text{NaAlSi}_3\text{O}_8$ and $\text{Na}_2\text{Si}_2\text{O}_5$ must be accommodated by high activity (fugacity) of SiF_4 . Therefore, the vapor pressure is very high at initial stages of devolatilization but decreases as the equilibrium (equation 23, Table 3) progresses to the right. It is also noteworthy that the relative abundance of gaseous species is rather insensitive to the bulk SiO_2 – Na_3AlF_6 proportions. According to calculations, SiF_4 remains the predominant gaseous species with increasing SiO_2 content up to tridymite saturation (see also Fig. 3).

Our thermodynamic calculations can also serve to interpret vapor-phase saturation in experiments. The intersection of the total vapor pressure and the experimental pressure (Fig. 4) defines a phase boundary, L (V), i.e. an equilibrium extent of devolatilization at the pressure of interest. When the total vapor pressure is lower than the confining pressure, the assemblage is vapor-undersaturated, i.e. in the L field. When the total vapor pressure is higher, a free vapor phase coexists with the liquid. The degrees of devolatilization at 100 MPa and 1 atm are shown in Fig. 4a and the corresponding mass changes in the fluorosilicate liquid in Fig. 4b. At 100 MPa, the extent of devolatilization is very small, and the changes in element concentrations in the melt are negligible (less than 0.05% relative). At 1 atm, the extent of devolatilization is greater, with weak SiO_2 (4.6%) and F (~0.15%) depletions and, consequently, Na_2O and Al_2O_3 enrichments (0.35% each).

This approach provides estimates of the compositional shifts in the liquid. In our study, we have limited all experiments to a maximum of 1100°C, as the magnitude of vaporization rises with temperature (Fig. 3). In addition, experiments were frequently performed at both

0.1 MPa and 100 MPa. Comparison of run products at the two pressures revealed no discrepancies.

EXPERIMENTAL AND ANALYTICAL METHODS

The silicate–fluoride melting equilibria were studied by quenching techniques and differential thermal analysis. Starting materials were synthetic glasses and pure natural minerals. Base glasses (HPG-2, AQ-1) represent compositions of the haplogranite minimum and the albite–quartz eutectic, respectively, at 100 MPa and H_2O saturation (Tuttle & Bowen, 1958). These were prepared by weighing of reagent-grade K_2CO_3 , Na_2CO_3 , Al_2O_3 and SiO_2 in desired proportions into an agate mortar, followed by grinding for 1 h under alcohol or acetone. The slurry was dried overnight and transferred to the platinum crucible. The mixture was decarbonated at a heating rate of 150°C/h and held at 1020°C for 8 h. Melting was carried out in several cycles (1 or 2 h) at 1400–1600°C with intermittent crushing. After each cycle, an aliquot of glass was analyzed by electron microprobe to verify alkali loss and to monitor compositional homogeneity. After the last melting, crushed chips were ground in an agate mortar for 1 h (dry) and the resulting glass powders were stored at 120°C until use. Starting crystalline phases were a mixture of quartz and tridymite (99.99 wt % SiO_2), natural albite (Amelia Court House, Virginia), natural topaz (Topaz Mountain, Utah), and natural cryolite (99.5%, Alfa Aesar). All substances were ground in an agate mortar (dry) and stored at 120°C. Compositions of all starting materials are given in Table 4. Starting mixes were prepared by weighing the base glasses and crystalline phases into an agate mortar and grinding for 1 h (dry). The as-weighed compositions are listed in Table 5 and are accurate to 0.1 wt %.

Experiments were performed in gold or platinum capsules depending upon the pressure–temperature conditions. Seamless tubing (Au: 2.0–2.2 mm OD; Pt: 3.0–4.0 mm OD) was cut into segments 10 mm long, cleaned in concentrated hydrofluoric acid, repeatedly rinsed with distilled water, ultrasonically cleaned with alcohol for 4 min, and annealed over the gas burner to yellow–orange heat. Capsules were flat-welded and loaded with starting materials (Au: 8–11 mg; Pt: 20–35 mg). For 1 atm experiments, the crimped capsules were stored at 300°C for 1 h to remove traces of moisture and welded immediately; the weight loss after heating was less than 0.3%.

Experiments were performed in tube furnaces (1 atm), cold-seal pressure vessels (up to 850°C, 100 MPa) or rapid-quench TZM pressure vessels (above 850°C, 100 MPa) with argon as a pressure medium. Temperatures were monitored by sheathed chromel–alumel

Table 4: Chemical composition of starting materials

Symbol	<i>n</i>	SiO ₂ (wt %)	Al ₂ O ₃	CaO	Na ₂ O	K ₂ O	F	Total	A/NK molar	Notes
HPG-2		79.47	11.73		3.90	4.91			1.00	
	16	78.37 (48)	11.53 (34)	0.0041 (53)	3.74 (13)	4.979 (94)		98.63 (24)	0.999 (36)	glass
AQ-1		81.56	11.47		6.97				1.00	
	10	82.10 (69)	11.62 (59)	0.0091 (99)	6.53 (35)	0.016 (12)		100.32 (54)	1.080 (80)	glass
albite		68.74	19.44		11.82				1.00	
	18	67.91 (34)	19.37 (12)	0.078 (57)	11.30 (12)	0.146 (21)		98.80 (35)	1.033 (13)	crystal
topaz		32.65	55.40				20.64			
	18	32.62 (39)	54.64 (28)	0.008 (10)	0.049 (79)	0.0071 (84)	20.92 (13)	99.44 (52)		crystal
cryolite			24.28		44.28		54.30		0.3333	
	10	0.011 (21)	25.65 (53)	0.012 (14)	45.67 (12)	0.010 (18)	57.29 (89)	104.51 (19)	0.3414 (71)	crystal

For each substance, first row indicates theoretical amounts and second row gives analysis by electron microprobe. Analytical conditions: accelerating voltage 15 kV, beam current 5 nA, beam diameter 20 μ m; *n*, number of analyzed points. Analytical totals are corrected for the fluorine-equivalent oxygen (the elevated total in the cryolite analysis is related to the correction procedure and has no effect on the element proportions). Standard deviations are reported as 1 σ . A/NK = molar Al₂O₃/(Na₂O + K₂O).

thermocouples, calibrated against the melting point of NaCl (800–7°C, Dawson *et al.*, 1963; Chase, 1998) and verified with a factory-calibrated thermocouple. Temperatures are accurate to $\pm 2^\circ\text{C}$ (tube furnaces and cold-seal vessels) and $\pm 5^\circ\text{C}$ (TZM vessels). Pressure was measured with Bourdon-tube gauges, calibrated against a factory-calibrated Heise gauge. Pressure measurements are accurate to ± 5 MPa and precise to ± 2 MPa. Experiments were quenched by either dropping the capsules from the 1 atm furnace into a cold-water bath (500°C/s), placing the cold-seal vessel into an air jet (150°C/min), or by free fall of the sample holder to the cooling collar in the TZM vessel (100°C/s). All capsules were checked for leakage, and charges were recovered immediately and stored at room conditions. Run products were studied optically in grain mounts and by electron microprobe; several chips from the same run were studied to avoid misinterpretation as a result of crystal settling. Large chips (0.5–1.5 mm) were mounted in epoxy, ground and polished in alcohol–oil mixtures, and carbon-coated for electron-microprobe analysis. All phase assemblages were verified by electron microprobe. Details of differential thermal analysis have been given by Dolejš & Baker (2006).

The time spans necessary to achieve equilibrium vary over several orders of magnitude in systems ranging from molten ionic salts (Na₃AlF₆) to fully polymerized silicates (NaAlSi₃O₈, SiO₂; Fig. 5). For cryolite, melting and crystallization occur within 6 and 2 min, respectively, as measured by differential thermal analysis. Experiments in the Na₃AlF₆–SiO₂ system, including quartz dissolution and tridymite growth, are reversible within less

than 60 min (Fig. 6a). In cryolite- and topaz-bearing systems, the formation of quench phases confirms that crystal nucleation has not been suppressed. Experiments across the silicate–fluoride join were usually carried out together to ensure identical run conditions, and consistency of their results from the silicate towards the fluoride end-member was verified. In the albite–quartz joins with fluorine-bearing minerals, different starting materials (aluminosilicate glasses vs crystalline albite and SiO₂) were used simultaneously to verify the invariance of experimental run products. Run durations in excess of 7 days were necessary in anhydrous systems near the SiO₂, albite–SiO₂ or haplogranite end-member. The lack of equilibrium is demonstrated by the presence of incompletely reacted starting materials or inhomogeneous melt compositions (measured by electron microprobe). These runs were not considered further and the compositional regions with disequilibrium were indicated in run tables and on phase diagrams by cross symbols without outline.

RUN PRODUCTS

We investigated a wide range of silicate to fluoride systems at temperatures between 520 and 1100°C. The overall appearance of the run products reflects nucleation and annealing rates related to individual phases, and growth rates that correlate with temperature. Run products contain stable equilibrium assemblages, but quench phases systematically occur in fluorine-rich compositions. Cryolite-rich or immiscible fluoride liquids did not

Table 5: Modal and chemical composition of base mixes

Symbol	Constituents			SiO ₂	Al ₂ O ₃	Na ₂ O	F ₂ O _{...1}	F	Al/(Na + K)	
	(wt %)			(wt %)					molar	
	<i>Silica</i>	<i>Cryolite</i>								
QC-15	85	15		85.000	3.643	6.643	4.715	8.144	0.333	
QC-60	40	60		40.000	14.570	26.570	18.859	32.577	0.333	
QC-90	10	90		10.000	21.856	39.856	28.289	48.866	0.333	
QC-96	4	96		4.000	23.313	42.513	30.175	52.134	0.333	
QC-98	2	98		2.000	23.798	43.398	30.803	53.210	0.333	
	<i>AQ-1</i>	<i>Cryolite</i>								
AQC-15	85	15		69.323	13.393	12.569	4.715	8.144	0.648	
AQC-60	40	60		32.623	19.159	29.360	18.859	32.577	0.397	
	<i>Silica</i>	<i>Albite</i>	<i>Cryolite</i>							
AQ8C-15	68	17	15	79.686	6.948	8.652	4.715	8.144	0.488	
AQ8C-60	32	8	60	37.499	16.126	27.516	18.859	32.577	0.356	
AQ4C-15	34.85	50.15	15	69.323	13.393	12.569	4.715	8.144	0.648	
AQ4C-60	16.4	23.6	60	32.623	19.159	29.359	18.859	32.577	0.397	
AC-15		85	15	58.429	20.168	16.687	4.715	8.144	0.735	
AC-60		40	60	27.496	22.347	31.298	18.859	32.577	0.434	
	<i>Silica</i>	<i>Topaz</i>	<i>Cryolite</i>							
TC-06		25.962	74.038	8.476	32.363	32.787	26.374	45.559	0.6	
TC-08		38.029	61.971	12.416	36.118	27.443	24.024	41.498	0.8	
TC-1		46.714	53.286	15.251	38.820	23.597	22.332	38.576	1.0	
TC-12		53.264	46.737	17.389	40.858	20.697	21.056	36.372	1.2	
QT-27	72.313	27.687		81.352	15.339		3.309	5.716	∞	
TCQ-1	54.956	21.042	24.002	61.826	17.486	10.629	10.059	17.376	1.0	
TCQ-2	28.925	11.075	60	32.541	20.706	26.570	20.183	34.864	0.474	
TCQ-3	23.373	35.796	40.832	35.059	29.747	18.082	17.112	29.560	1.0	
TCQ-4	15.801	24.199	60	23.701	27.977	26.570	21.751	37.573	0.640	
TCQ-5	10	42.043	47.958	23.726	34.938	21.238	20.099	34.718	1.0	
TCQ-6	27.651	42.349	30	41.477	30.747	13.285	14.491	25.031	1.407	
	<i>Silica</i>	<i>Albite</i>	<i>Topaz</i>	<i>Cryolite</i>						
ATC-1		39.961	28.047	31.993	36.626	31.076	18.890	13.408	23.161	1.0
ATCQ-1	30.688	44.160	11.750	13.403	64.879	18.350	11.154	5.617	9.703	1.0
ATCQ-2	48.318	12.079	18.500	21.103	62.661	17.722	10.773	8.844	15.277	1.0
ATCQ-3	16.4	23.6	12	48	36.540	22.893	24.045	16.521	28.539	0.579
	<i>AQ-1</i>	<i>Topaz</i>	<i>Cryolite</i>							
AQTC-05	95	2.336	2.664	78.242	12.838	7.804	1.117	1.929	1.0	
AQTC-10	90	4.671	5.329	74.926	14.206	8.635	2.233	3.858	1.0	
AQTC-40	60	18.686	21.314	55.034	22.410	13.622	8.933	15.430	1.0	
AQTC-60	40	28.028	31.972	41.773	27.880	16.945	13.399	23.146	1.0	
AQTC-69	30.955	32.254	36.791	35.776	30.354	18.451	15.419	26.635	1.0	

form glasses and quenched to aggregates of solid phases (cryolite, sodium aluminosilicates; Fig. 6b). The proportion of quench aluminosilicates allows approximate estimation of the silicate components in the fluoride melt, which do not exceed ~5 vol. %. On the other hand, fluorine-poor liquids quench to homogeneous glasses. At ~10 wt %

F in the melt, quench cryolite starts to appear in the form of branching aggregates, elongate dendritic rods (up to 200 µm long, Fig. 6c) or micrographic intergrowths with aluminosilicate glass (10–80 µm). Above ~25 wt % F, liquids quench to an inhomogeneous aggregate of cryolite grains, aluminosilicate phases and glass.

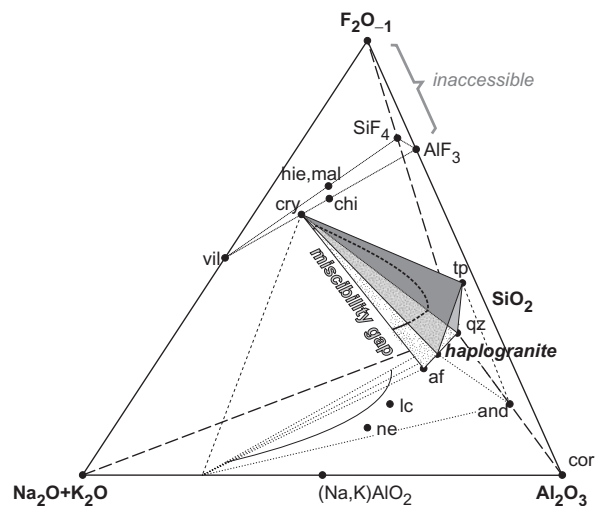


Fig. 5. Location of the experimentally studied joins and sections in the quaternary system $(\text{Na}_2\text{O} + \text{K}_2\text{O})\text{-Al}_2\text{O}_3\text{-SiO}_2\text{-F}_2\text{O}_{-1}$. The three-dimensional topology with the schematic extent of the liquid–liquid miscibility gap is projected onto the fluorine-free base to illustrate changes in silica content and peralkalinity or peraluminosity.

Stable cryolite forms large round grains ($10\text{--}70\ \mu\text{m}$) at all conditions (Fig. 6d and e) and can easily be distinguished from dendritic or micrographic cryolite that formed during quenching. These large cryolite grains are optically isotropic, single crystals with a stoichiometric composition and no quench-related inclusions. In several composition sections, experiments were performed slightly above the cryolite melting temperature to check for the different appearance of the liquid–liquid immiscibility (Fig. 6b).

Topaz develops subhedral crystal shapes and has a uniform grain size ($10\text{--}30\ \mu\text{m}$); incomplete dissolution of topaz is revealed by angular morphologies and irregular fragment sizes. Alkali feldspar occurs as minute anhedral grains ($10\ \mu\text{m}$) and its morphology tends to evolve to elongate laths ($20\text{--}40\ \mu\text{m}$ long) with increasing alkali or fluorine contents. The morphology of the silica polymorphs (quartz and tridymite) and their grain size are closely related to run temperature. Tridymite forms large subhedral grains with planar crystal faces ($5\text{--}40\ \mu\text{m}$; Fig. 6e and f) or thin laths ($30\text{--}90\ \mu\text{m}$ long). In contrast, quench silica polymorphs in cryolite-rich melts form minute round grains ($2\text{--}5\ \mu\text{m}$). Stable quartz occurs as subhedral prismatic grains ($\sim 10\ \mu\text{m}$) and it becomes round and fine-grained (less than $5\ \mu\text{m}$) with decreasing temperature. Failure to attain equilibrium in fluorine-poor and silica-rich compositions can be identified by the presence of fragments of starting phases.

In all joins, the geologically relevant liquid lines of descent evolve to fluorine-rich residual melt compositions. The presence of quench phases, the decreasing amount

of interstitial melt and the small grain size at low temperatures severely limit the systematic use of electron microprobe techniques for measuring the compositions of volatile-rich melts. Therefore, we have systematically studied binary and ternary sections and derived phase-diagram topologies by chemography.

THE SILICA-CRYOLITE SYSTEM

Liquidus relations in the $\text{SiO}_2\text{-Na}_3\text{AlF}_6$ system are the starting point for the general topology of silicate–fluoride systems (Table 6) and have additional applications to the study of cryolite attack on SiO_2 -based refractories during aluminum electrolysis (Snow & Welch, 1972; Siljan *et al.*, 2001). In previous studies, the location of the eutectic and the presence of the fluoride–silicate liquid–liquid immiscibility have been controversial (Weill & Fyfe, 1964; Grjotheim *et al.*, 1971; Kogarko & Krigman, 1975, 1981). This binary system is characterized by a large stability field of silica polymorphs (quartz, tridymite; Fig. 7). This has been verified by a reversed run (number 34; Fig. 6a) with quartz single crystal surrounded by cryolite powder (50 wt % each). The run was placed at 1020°C and 1 atm for 1 h, then reversed to 935°C , kept at this temperature for 24 h and quenched. Its texture reveals the initial dissolution of quartz in the cryolite melt, followed by tridymite growth during cooling. These observations confirm not only the rapid approach to equilibrium but also provide unambiguous evidence for its location in the $\text{SiO}_2 + \text{liquid}$ field, which was hitherto unclear. The binary eutectic is located at ~ 95 wt % cryolite, at 999°C (1 atm) and 1015°C (100 MPa), determined by differential thermal analysis.

The asymmetric location of the binary eutectic can be explained by the disparate melting temperatures of silica and cryolite, augmented by strong positive deviations from ideality as a result of coordination differences (Dolejš & Baker, 2005). The location of the cryolite–silica eutectic on the cryolite side of the phase diagram is in contrast to other cryolite–silicate systems (Rutlin, 1998; Rutlin & Grande, 1999). The present experiments did not intersect the fluoride–silicate miscibility gap below 1100°C (Fig. 7), but the liquid–liquid immiscibility in the $\text{SiO}_2\text{-Na}_3\text{AlF}_6$ binary has been documented at 1200°C and 1 atm (Kogarko & Krigman, 1975) and at 1200°C and 600 MPa (G. Robert & D. Dolejš, unpublished experimental results).

THE SILICA-ALBITE-CRYOLITE SYSTEM

The silica–albite–cryolite system serves as a model for peralkaline fluorine-bearing granites and rhyolites. The albite–cryolite binary has a very similar topology to the silica–cryolite binary, but the eutectic position

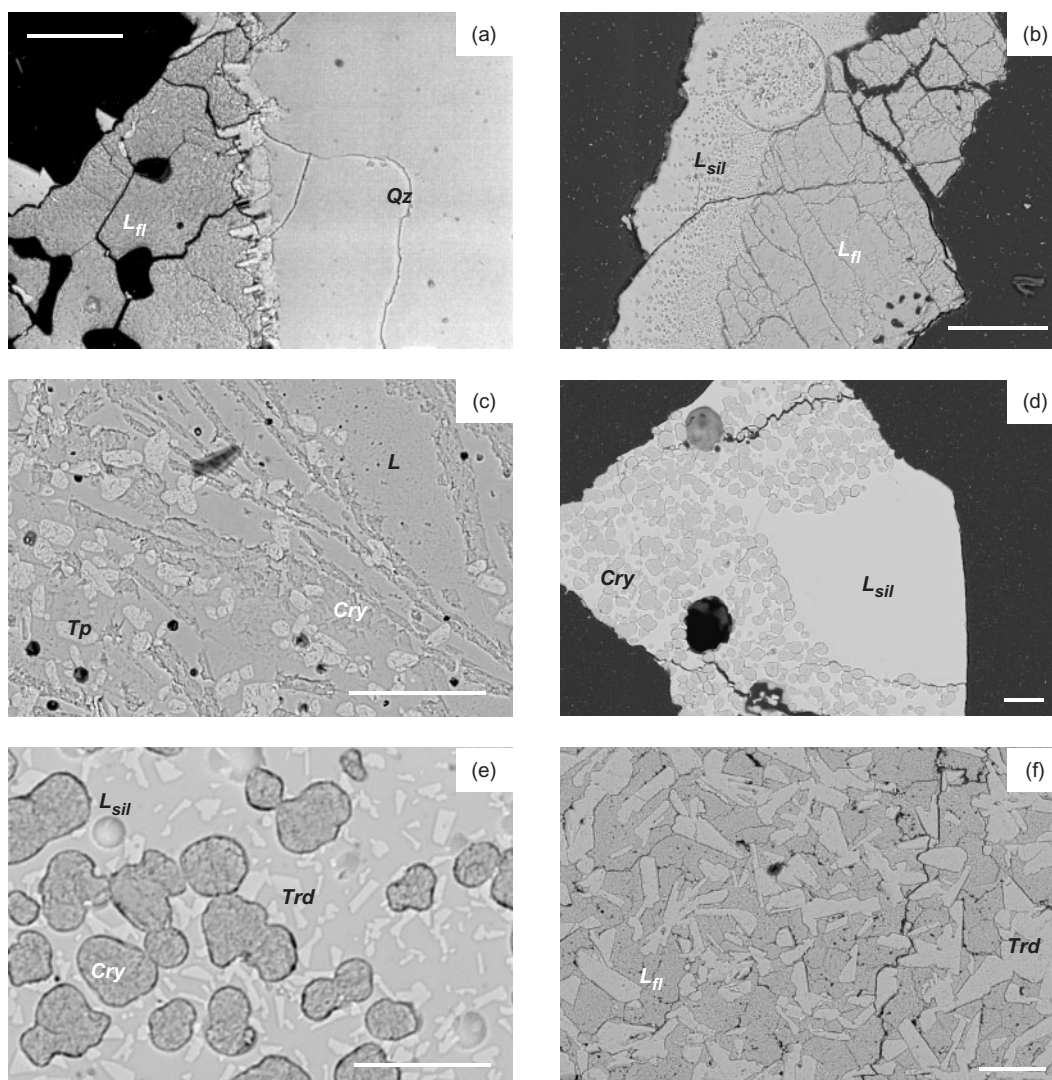


Fig. 6. Back-scattered electron images of experimental run products (all scale bars represent 100 μm): (a) reversal of quartz dissolution and crystallization in a cryolite melt: small crystals represent overgrowths on the quartz–liquid interface, produced during a temperature decrease (run 341, 1020–935°C, 1 atm); (b) fluoride–silicate liquid–liquid immiscibility: the immiscible liquids are completely separated—fluoride liquid (right part) is quenched to massive cryolite with rare round quench aluminosilicates, silicate liquid (left part) is preserved as glass with quench immiscibility (unmixing of fluoride before the glass transition; run 572, 1040°C, 100 MPa); (c) oval topaz crystals in fluorine-rich silicate liquid (glass) and long dendritic rods of quench cryolite (run 344, 700°C, 100 MPa); (d) settling of cryolite crystals along the capsule bottom (run 590, 900°C, 1 atm); (e) round cryolite crystals and subhedral tridymite crystals in the silicate liquid (glass): cryolite grains do not contain quench aluminosilicate phases, i.e. cannot represent immiscible fluoride globules (run 356, 900°C, 1 atm) (see text for details); (f) euhedral tridymite crystals in non-quenchable Na_3AlF_6 – SiO_2 liquid (run 594, 1100°C, 100 MPa).

is reversed to low fluorine contents (Rutlin, 1998; Siljan *et al.*, 2001).

We studied this ternary system along two parallel sections with 15 and 60 wt % cryolite, respectively, each from the SiO_2 to the albite side of the ternary and spaced to provide additional joins from cryolite to $\text{Qz}_{80}\text{Ab}_{20}$ and $\text{Qz}_{41}\text{Ab}_{59}$ by weight, respectively (Fig. 8, Table 4); the $\text{Qz}_{41}\text{Ab}_{59}$ composition represents the albite–quartz eutectic at 100 MPa and H_2O saturation (Tuttle & Bowen, 1958). The polybaric temperature–composition sections at 15 wt % and 60 wt % cryolite,

respectively (Fig. 9a and b), are characterized by fluoride–silicate liquid–liquid immiscibility above 970°C (1 atm and 100 MPa). The miscibility gap is underlain by fields containing cryolite, silica polymorphs and/or albite, which coexist with fluorine-poor silicate liquid.

The fluoride–silicate miscibility gap extends over the entire ternary system. It is located on silica liquidus in the SiO_2 -rich portion of the ternary, but it overlies the cryolite liquidus in the albite-rich part. Consequently, the location of binary eutectics shifts from the high-fluorine contents (95 wt % cry + 5 wt % SiO_2) to low

Table 6: *Experimental results in the system silica–albite–cryolite*

Run	Mix	Pressure (MPa)	Temperature (°C)	Duration (h)	Assemblage	Notes
595	QC-15	100	1100	2.3	L + trd	
318	QC-15	0.1	1050	7.0	L + trd	
297	QC-15	0.1	1020	20	L + trd	
347	QC-15	0.1	960	281.4	subsolidus	
306	QC-15	0.1	900	169.1	subsolidus	
594	QC-60	100	1100	2.3	L + trd	
319	QC-60	0.1	1050	7.0	L + trd	
573	QC-60	100	1040	5.0	L + qz	
296	QC-60	0.1	1020	20	L + trd	
348	QC-60	0.1	960	281.4	subsolidus	
305	QC-60	0.1	900	169.1	subsolidus	
574	QC-90	100	1040	3.5	L + trd	
349	QC-90	0.1	900	281.4	subsolidus	
616	QC-96	0.1	1003	22.0	L + cry	
617	QC-98	0.1	1003	22.0	L + cry	
350	AQ8C-15	0.1	1020	73.8	L _{sil} + L _{fl} + trd	
351	AQ8C-15	0.1	900	121.1	L + trd + cry	
353	AQ8C-60	0.1	1020	73.8	L _{sil} + L _{fl} + trd	
510	AQ8C-60	0.1	960	52.9	L + trd + cry	
352	AQ8C-60	0.1	900	121.1	L + trd + cry	
507	AQ4C-15	0.1	960	52.9	L + cry	
557	AQ4C-15	0.1	900	121.2	L + cry	
569	AQ4C-15	100	780	194.8	L + qz + cry	incipient melting
585	AQ4C-15	100	760	170.4		incipient, incomplete melting
572	AQ4C-60	100	1040	5.0	L _{sil} + L _{fl}	
615	AQ4C-60	100	900	90.8	L + cry	
556	AQ4C-60	0.1	900	121.2	L + cry	
314	AQC-15	0.1	1050	7.0	L	
299	AQC-15	0.1	1020	20	L	
508	AQC-15	0.1	960	52.9	L + cry	
308	AQC-15	0.1	900	169.1	L + cry	
304	AQC-15	100	800	169.2	L + qz + cry	
568	AQC-15	100	780	194.8	L + qz + cry	small amount of glass
317	AQC-60	0.1	1050	7.0	L _{sil} + L _{fl}	quench cryolite
509	AQC-60	0.1	960	52.9	L + cry	
307	AQC-60	0.1	900	169.1	L + cry	
302	AQC-60	100	800	169.2	L + qz + cry	small amount of glass
320	AQC-60	0.1	700	173.9	subsolidus	no melting
529	AC-15	0.1	1020	52.8	L	
519	AC-15	0.1	960	53.1	L	
555	AC-15	0.1	900	121.2	L + cry	
570	AC-15	0.1	880	122.2	ab + cry	subsolidus, no melting
571	AC-60	100	1040	5.0	L	quench immiscibility
528	AC-60	0.1	1020	52.8	L _{sil} + L _{fl}	
614	AC-60	100	960	90.8	L + cry	
518	AC-60	0.1	960	53.1	L + cry	
554	AC-60	0.1	900	121.2	L + cry	

SiO₂ polymorphs are interpreted according to Kennedy *et al.* (1962) and Ostrovsky (1966).

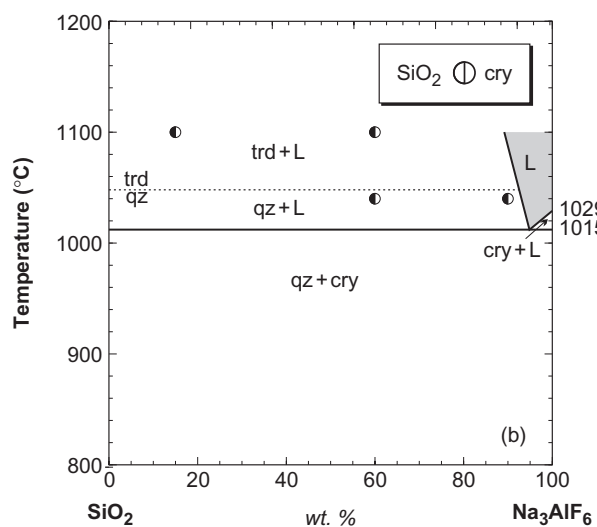
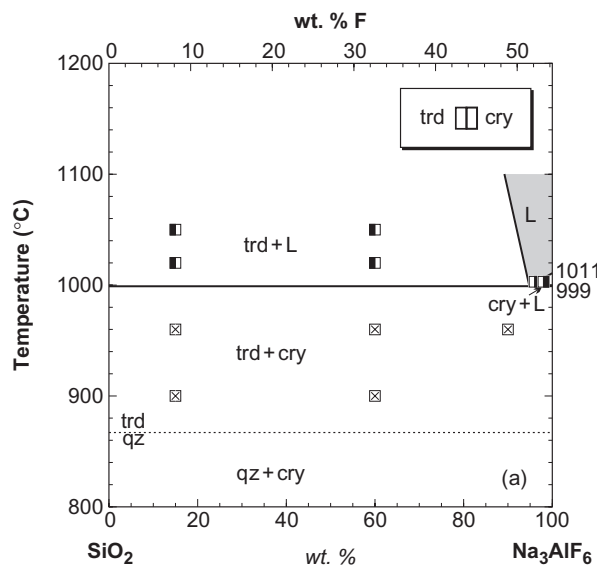


Fig. 7. Phase diagrams of the silica-cryolite systems at 1 atm (a) and 100 MPa (b). The cryolite-quartz/tridymite eutectic is located near the cryolite composition, in contrast to other silicate-cryolite systems (Rutlin, 1998). Temperatures of cryolite and cryolite-SiO₂ melting were determined by differential thermal analysis (see Dolejš & Baker, 2006).

fluorine contents (<15 wt % cry + >85 wt % ab). Hence, finding the ternary albite-quartz-cryolite eutectic is fundamentally important for the maximum solubility of fluorine in peralkaline granitic melts and the accessibility of the fluoride-silicate liquid-liquid immiscibility to natural melts. In Fig. 9a, the down-temperature sequence of the stability fields in the vicinity of Ab₅₉Qz₄₁ is: L_{sil}, L_{sil} + cry and L_{sil} + cry + SiO₂. That is, liquid with 15 wt % Na₃AlF₆ will first saturate with cryolite, and subsequent crystallization will drive liquid compositions away from the cryolite apex towards lower fluorine contents.

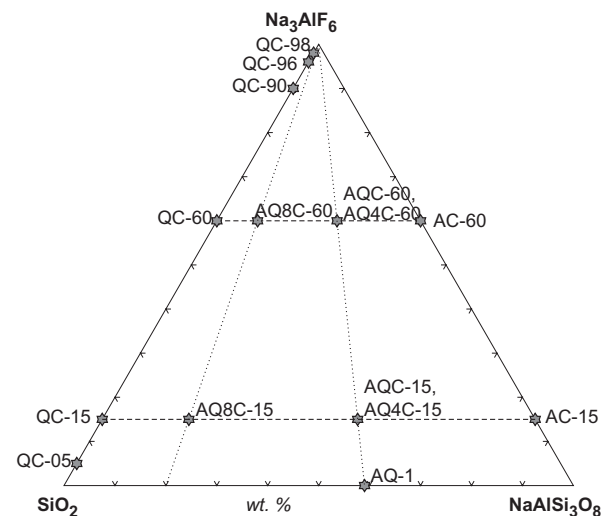


Fig. 8. Starting compositions in the silica-cryolite-albite system.

All lower-temperature features, the SiO₂-cry cotectic and the SiO₂-ab-cry eutectic, must lie at less than 15 wt % cryolite.

The experimental results in the 15%-cryolite section allow for two distinct phase-diagram topologies, depending on the location of the qz/trd-cry-L_{sil} (L_{fl}) invariant point with respect to the investigated section (Fig. 9a). If the invariant point occurs at greater than 15 wt % cryolite, the sequence with increasing albite content of high-temperature fields will be SiO₂ + L_{fl}, SiO₂ + L_{fl} + L_{sil}, SiO₂ + L_{sil} and L_{sil}; the field L_{fl} + L_{sil} will occur at very high temperatures only and the field cry + L_{fl} + L_{sil} will not exist. If the invariant point occurs at less than 15 wt % cryolite, the sequence of phase fields will be SiO₂ + L_{fl}, SiO₂ + L_{fl} + L_{sil}, L_{fl} + L_{sil} and L_{sil} (Fig. 9a). The second interpretation is preferred, as other invariant points, albite-quartz-cryolite and albite-cryolite eutectics, occur at less than 15 wt % cryolite as well. We emphasize that this choice does not affect the overall topology of the ternary system as it only concerns the relative position of an invariant point with respect to the composition section chosen for experimental work.

The liquidus relations in the SiO₂-NaAlSi₃O₈-Na₃AlF₆ ternary are summarized in Fig. 10. The silica-cryolite cotectic represents a divide (thermal minimum) for the fluoride-silicate miscibility gap at ~970°C (1 atm and 100 MPa). The ternary quartz-albite-cryolite eutectic occurs at ~5 wt % F and ~770°C (100 MPa). Peralkaline fluorine-bearing silicic magmas will fractionate along the quartz-albite cotectic with progressively increasing fluorine content in the melt until they reach the quartz-albite-cryolite eutectic and completely crystallize. As the fluoride-silicate miscibility gap is located on the cryolite

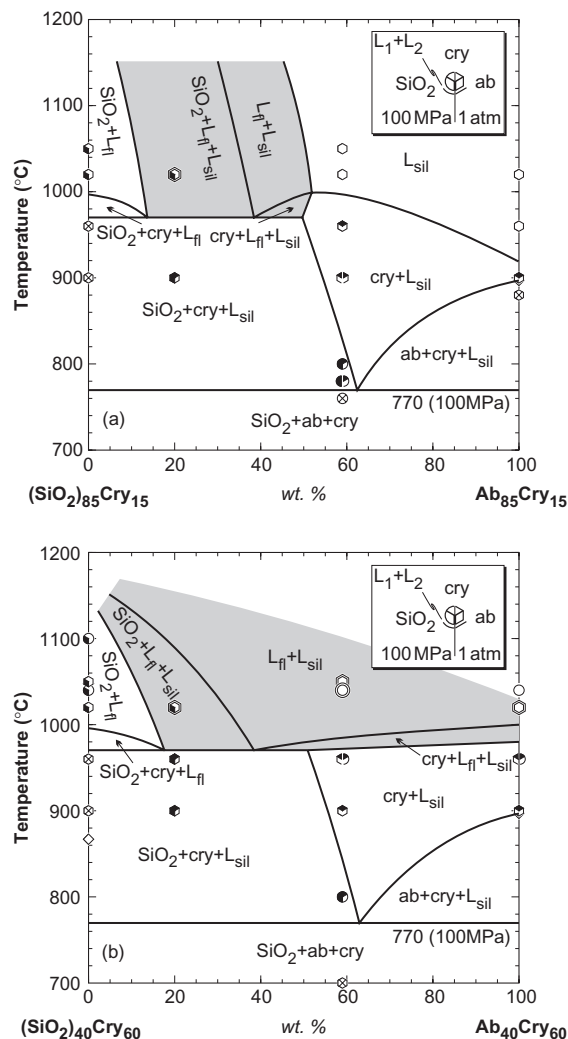


Fig. 9. Temperature-composition sections through the silicate-cryolite-albite system. (a) Polybaric section of the silica-albite join with 15 wt % cryolite; (b) polybaric section of the silica-albite join with 60 wt % cryolite. The fluoride-silicate liquid-liquid immiscibility extends over the entire ternary system and closes at 970°C at the L_{sil} ($L_{fl} + SiO_2 + cry$) invariant point. The ternary quartz-albite-cryolite is located at 770°C and 100 MPa.

liquidus in this region, the liquid-liquid immiscibility is inaccessible to peralkaline quartz-feldspar-precipitating melts.

THE SILICA-TOPAZ-CRYOLITE SYSTEM

Topaz is a common mineral in peraluminous fluorine-bearing granites, rhyolites and their differentiation products (ongonites and quartz topazites). From the thermodynamic viewpoint, topaz and cryolite are products of the first fluorination steps of feldspars (Fig. 2; equation 10, Table 3). Therefore, these minerals are

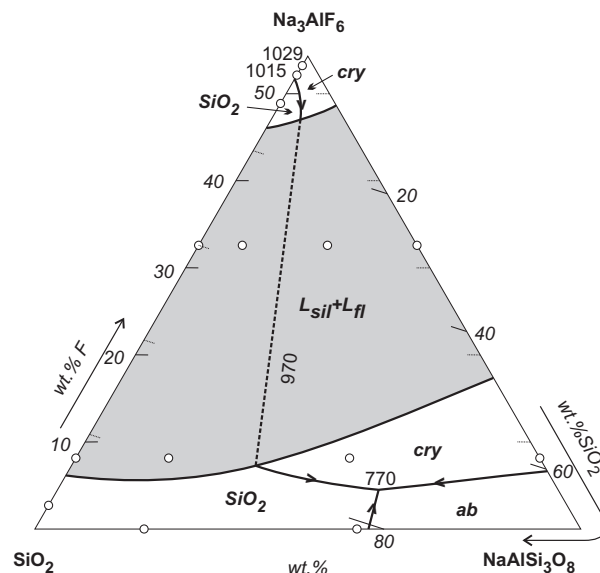


Fig. 10. Liquidus projection of the silica-albite-cryolite ternary system at 100 MPa. The fluoride-silicate miscibility gap extends from the silica liquidus (in the silica-cryolite binary) to the cryolite liquidus (in the albite-rich portion of the diagram). The albite-quartz cotectic leads to the ternary eutectic at 770°C and does not reach the miscibility gap. $\circ$, locations of starting compositions. Concentrations of SiO_2 and F are shown on the sides.

potential fluorine buffers during crystallization of granitic and rhyolitic rocks. The SiO_2 - $Al_2SiO_4F_2$ - Na_3AlF_6 system covers a wide range of peralkaline to peraluminous compositions and is pierced by the albite- F_2O_{-1} and nepheline- F_2O_{-1} joins (Fig. 11). If a stability field of albite and/or nepheline was found in the silica-topaz-cryolite ternary, this would indicate the existence of the peritectic transition: alkali feldspar/feldspathoid + liquid $\rightarrow$ cryolite/chiolite + topaz + quartz. Such a peritectic point would allow for very high fluorine enrichments in residual melts and the formation of feldspar-free eutectic assemblages (compare quartz topazites).

We studied several composition sections (isopleths) in this ternary (Fig. 11; Tables 7 and 8); the subaluminous SiO_2 - $Tp_{47}Cry_{53}$ section divides the peralkaline and peraluminous space, respectively, and intersects the other three joins at the following compositions: albite- F_2O_{-1} (TCQ-1), nepheline- F_2O_{-1} (TCQ-3) and cryolite-topaz (cation Al/Na = 1; TC-1).

The phase diagram for the cryolite-topaz binary at 100 MPa is presented in Fig. 12. This system is characterized by simple binary behavior with a eutectic at 770°C (39.2 wt % F, cation Al/Na $\sim$ 0.95). In the topaz-cryolite-silica ternary, the temperature-composition sections cryolite- $(SiO_2)_{73}Tp_{27}$ and silica-topaz with 60 wt % cryolite (Fig. 13) both intersect the field of the silicate-fluoride liquid-liquid immiscibility, which extends from the SiO_2 - Na_3AlF_6 binary. The two-liquid field is

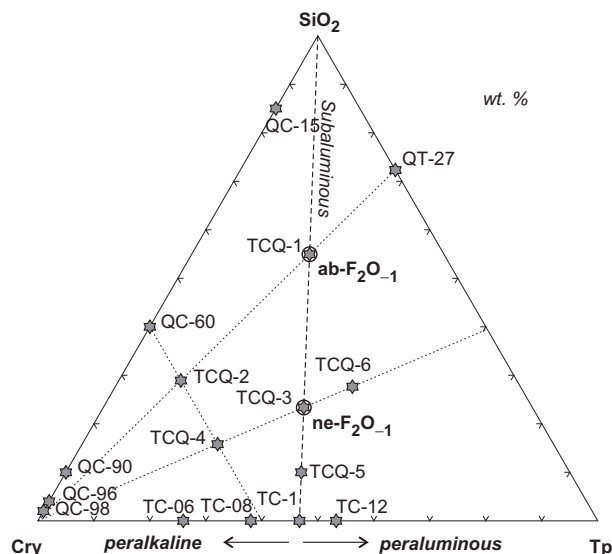


Fig. 11. Starting compositions in the silica-cryolite-topaz system. This system is pierced by tie-lines corresponding to fluorination of albite, $\text{ab-F}_2\text{O}_{-1}$ ($\text{NaAlSi}_3\text{O}_6\text{F}_{2.67}$, TCQ-1), and nepheline, $\text{ne-F}_2\text{O}_{-1}$ ($\text{NaAlSiO}_2\text{F}_{2.67}$, TCQ-3). The SiO_2 -TC-1 section separates the peralkaline and peraluminous space of the diagram.

underlain by the ternary assemblage $\text{SiO}_2 + \text{L}_{\text{sil}} + \text{L}_{\text{fl}}$ and is located exclusively on the tridymite/quartz liquidus. The miscibility gap closes at 960°C , and it is not intersected by the silica-cryolite or silica-topaz cotectic curves. The large temperature interval (1000 – 740°C), occupied by silica- and/or cryolite-bearing fields (Figs 13 and 14) indicates prolonged existence of liquids migrating from high-temperature binary eutectics (silica-cryolite and silica-topaz, Fig. 7, Table 8) towards the ternary quartz-topaz-cryolite eutectic.

This ternary quartz-topaz-cryolite system does not contain any additional (pseudoternary) phases (e.g. albite or nepheline). Thus the silica-topaz-cryolite system represents a thermal barrier in the Na_2O – Al_2O_3 – SiO_2 – F_2O_{-1} composition space, and the stability fields of the ‘high-fluorination’ phases (chiolite, maladrite) are not accessible through magmatic fractionation.

Changes in composition of residual fluorine-rich liquids are illustrated by the liquidus projection of the SiO_2 – $\text{Al}_2\text{SiO}_4\text{F}_2$ – Na_3AlF_6 ternary (Fig. 14). In this diagram, the system aluminosity (cation Al/Na ratio) increases from the left to the right and fluorine concentrations increase towards the base. Cotectic curves converge to the ternary eutectic with composition $\text{Qz}_{19}\text{Cry}_{45}\text{Tp}_{36}$ (31.9 wt % F, $\text{Al}/\text{Na} \sim 0.95$), located at 740°C (100 MPa). It is instructive to compare the changes of the eutectic location in several cryolite-bearing binaries. In the cryolite-silica binary, the eutectic occurs close to the cryolite end-member at 1015°C and 100 MPa (Fig. 7). In the cryolite-albite binary, the eutectic occurs close to

Table 7. Experimental results in the system cryolite-topaz

Run	Mix	Pressure (MPa)	Temperature ($^\circ\text{C}$)	Duration (h)	Assemblage	Notes
434	TC-08	100	800	175.7	L + cry	quench crystals
409	TC-08	100	770	170.7	L + cry + tp	incipient melting
281	TC-1	0.1	900	167.5	L	
435	TC-1	100	800	175.7	L	quench crystals
408	TC-1	100	770	170.7	cry + tp	no melting
375	TC-1	100	750	165.2	cry + tp	no melting
346	TC-1	100	700	327.6	cry + tp	no melting
436	TC-12	100	800	175.7	L + tp	quench crystals
407	TC-12	100	770	170.7	cry + tp	no melting
376	TC-12	100	750	165.2	cry + tp	no melting

the silicate end-member (900°C , 1 atm), and the liquid-liquid miscibility gap is inaccessible to the albite-saturated liquid line of descent (Fig. 10). In the cryolite-topaz binary, the eutectic is located in the center of the join (770°C , 100 MPa), without the liquid-liquid immiscibility (Fig. 12). The interactions of these four phases (quartz, albite, topaz and cryolite) control the course of differentiation in the ‘fluorohaplogranite’ system. Increasing melt aluminosity as a result of the addition of topaz causes the miscibility gap to close near the subaluminous composition (Fig. 14), and the paths of cotectic crystallization converge to high fluorine enrichment owing to the strong temperature depression near the cryolite-topaz join.

THE SILICA-ALBITE-TOPAZ-CRYOLITE SYSTEM

The quaternary silica-albite-topaz-cryolite system represents an analogue for the fluorine-bearing granites and rhyolites. In this section, we synthesize the course of liquid lines of descent of quartz-feldspar-precipitating melts with variable alkali/aluminum ratios.

Melting equilibria in the silica-albite-cryolite system reveal that the fluoride-silicate miscibility gap is located on the cryolite liquidus and therefore inaccessible to fractionating peralkaline melts (Fig. 10). On the other hand, the liquidus relations in the silica-topaz-cryolite system indicate the down-temperature extension of the fluoride-silicate liquid immiscibility to subaluminous conditions (Fig. 14). To resolve the termination of the immiscibility for low-temperature subaluminous conditions in the presence of albite, the central portion of the quaternary system has been studied along two pseudo-binary sections (Fig. 15): the subaluminous section starts from TCQ-1 (Table 5; Fig. 11) by adding albite (ATCQ-2,

Table 8: *Experimental results in the system silica–cryolite–topaz*

Run	Mix	Pressure (MPa)	Temperature (°C)	Duration (h)	Assemblage	Notes
575	TCQ-1	100	1040	3.5	L _{sil} + L _{fl}	
586	TCQ-1	100	960	90.8	L + qz	
504	TCQ-1	0.1	960	51.6	L + trd	
279	TCQ-1	0.1	900	167.5	L + trd	
599	TCQ-1	100	840	164.8	L + qz	relics of topaz (rare)
157	TCQ-1	100	800	211.1	L + tp (+ qz)	relics of silica
251	TCQ-1	0.1	750	173.6	L + qz	no equilibrium
254	TCQ-1	0.1	720	166.1	L + qz	no equilibrium, small amount of glass
150	TCQ-1	100	700	169.3		no melting
576	TCQ-2	100	1040	3.5	L _{sil} + L _{fl}	quench crystals
355	TCQ-2	0.1	1020	73.8	L _{sil} + L _{fr} + trd	quench crystals
587	TCQ-2	100	960	90.8	L + qz + cry	quench crystals
525	TCQ-2	0.1	960	53.1	L + trd + cry	quench crystals
310	TCQ-2	0.1	900	169.1	L + trd + cry	quench crystals
411	TCQ-2	100	840	22.5	L + qz + cry	quench crystals
300	TCQ-2	100	800	169.2	L + qz + cry	quench crystals
252	TCQ-2	0.1	750	173.6	L + qz + cry	quench crystals
262	TCQ-2	0.1	720	166.1	L + qz + cry	quench crystals
277	TCQ-3	0.1	900	167.5	L	
412	TCQ-3	100	840	22.5	L	relics of crystals
273	TCQ-3	100	800	169.5	L	
531	TCQ-4	0.1	1020	52.8	L	quench crystals
526	TCQ-4	0.1	960	53.1	L	quench crystals
558	TCQ-4	0.1	900	121.2	L + cry	quench crystals
414	TCQ-4	100	840	22.5	L + cry + qz	quench crystals
377	TCQ-4	100	750	165.2	L + cry + qz	quench crystals
415	TCQ-4	100	730	169.8	subsolidus	no melting
378	TCQ-5	100	750	165.2	L + tp (+ cry)	quench crystals
416	TCQ-5	100	730	169.8	subsolidus	no melting
593	TCQ-6	100	960	90.8	L + tp	
600	TCQ-6	100	840	164.8	L + tp	quench crystals
379	TCQ-6	100	750	165.2	L + qz + tp	
417	TCQ-6	100	730	169.8	subsolidus	no melting
596	QT-27	100	1100	2.3	L + tp	

ATCQ-1) and the 60 wt %-cryolite isopleth, which emanates from peralkaline AQC-60 (Table 5; Fig. 8) by adding topaz until it reaches the subaluminous composition (ATCQ-3, Fig. 15). This approach allowed us to constrain liquidus and cotectic surfaces in the anhydrous quaternary system (Fig. 16).

All experimental results from binary, ternary and quaternary sections under anhydrous conditions (Tables 5–9) are combined in the liquidus projection in Fig. 16. This anhydrous four-component system consists of four liquidus volumes (quartz, albite, topaz and cryolite)

and one liquid miscibility gap that extends continuously from the quartz stability field to the cryolite field. Liquid lines of descent follow cotectic surfaces and curves and their relationship to the miscibility gap determines the relevance of liquid–liquid immiscibility for geological compositions. The subaluminous plane (through the tetrahedron, Fig. 16) separates the peraluminous and peralkaline composition spaces and intersects the albite–quartz–topaz cotectic ($E_{\text{AQT}}-E_{\text{AQTc}}$ curve, Fig. 16), in agreement with location of the quaternary albite–quartz–topaz–cryolite eutectic (E_{AQTc} point) at a weakly

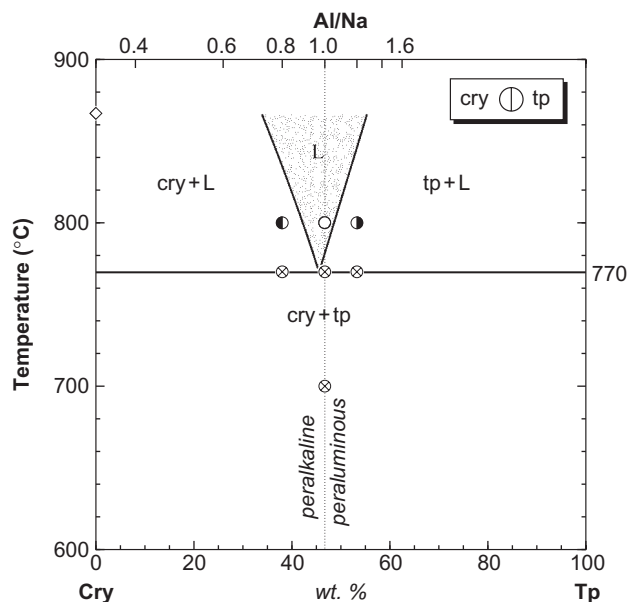


Fig. 12. Phase diagram of the cryolite–topaz system at 100 MPa. The binary eutectic is located at 770°C and the cation ratio Al/Na $\sim$ 1.

peralkaline composition. With decreasing temperature ($<700^\circ\text{C}$), melting in the anhydrous quartz–albite–topaz–cryolite system becomes extremely sluggish and the runs do not reach equilibrium in a reasonable time span. Therefore, a more accurate location and temperature of the anhydrous quaternary eutectic was not determined experimentally. This problem was eliminated by determining phase equilibria in the same system at hydrous conditions in our companion study (Dolejš & Baker, 2007).

Natural silicic magmas with low fluorine contents plot close to the albite–quartz binary eutectic (E_{AQ_2} , Fig. 16). Magmatic fractionation of quartz and albite will place the liquid compositions on the quartz–albite cotectic surface, and depending on their initial alkali/aluminum ratio, the fractionation of quartz and albite will promote their peralkaline or peraluminous character. Peralkaline melts will reach the cryolite saturation surface and subsequently follow the albite–quartz–cryolite cotectic curve whereas peraluminous melts will saturate with topaz and further evolve along the albite–quartz–topaz cotectic curve. Whereas both ternary cryolite- or topaz-bearing ternary eutectics (E_{AQC} , E_{AQT}) are located at relatively low fluorine contents (less than 5 wt % F), the quaternary eutectic (E_{AQTC}) is displaced to much higher fluorine levels. Therefore, the evolving melts, upon reaching cryolite or topaz saturation, will continue to fractionate along the univariant curves to high levels of fluorine enrichment (towards E_{AQTC}) and their alkali/aluminum ratios will converge. In the absence of other rock-forming minerals (micas, aluminosilicates), which buffer the melt alumina saturation index

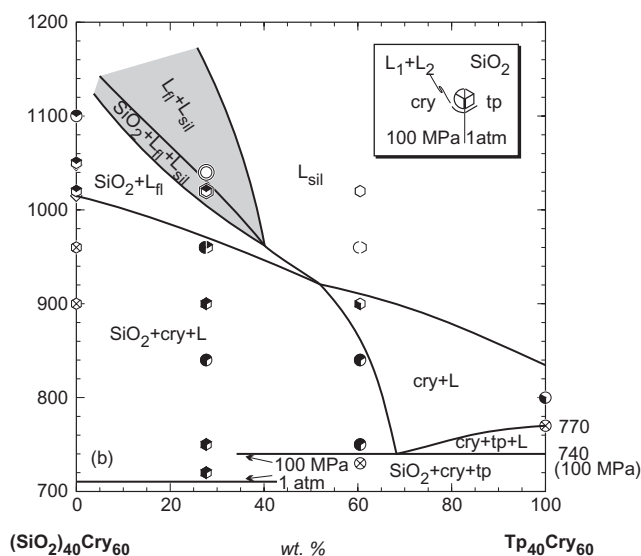
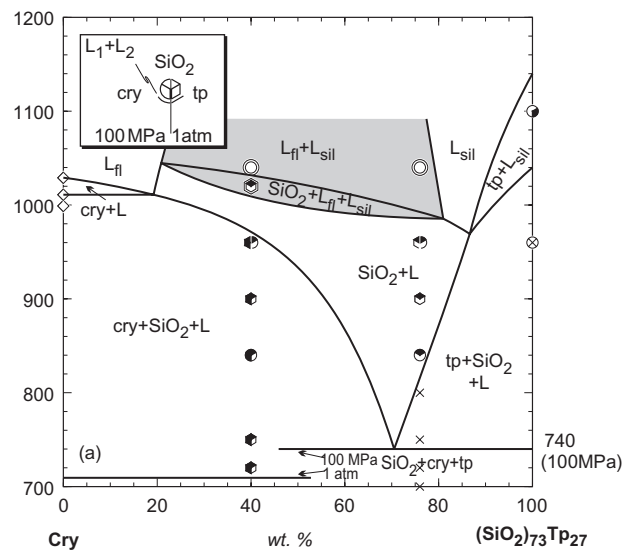


Fig. 13. Temperature–composition sections through the silica–cryolite–topaz system. (a) Polybaric section of the cryolite–(SiO_2)₇₃Tp₂₇ join. $\times$, experiments that did not attain the equilibrium. (b) Polybaric section of the silica–topaz join with 60 wt % cryolite (bulk composition TC-08 serves as a proxy for the Tp₄₀Cry₆₀ end-member). The fluoride–silicate liquid–liquid immiscibility is located above 960°C and it does not reach the quartz–cryolite or quartz–topaz cotectic surface.

(Shand, 1927), the initial peralkaline or peraluminous trends will be reversed by topaz or cryolite saturation, respectively, and the residual melts will converge to a very weakly peralkaline quaternary eutectic. The fluoride–silicate miscibility gap is completely confined to quartz and cryolite stability volumes and it does not penetrate the albite–cryolite cotectic surface. The fluoride–silicate miscibility gap is thus not accessible to any feldspar-precipitating liquid line of descent.

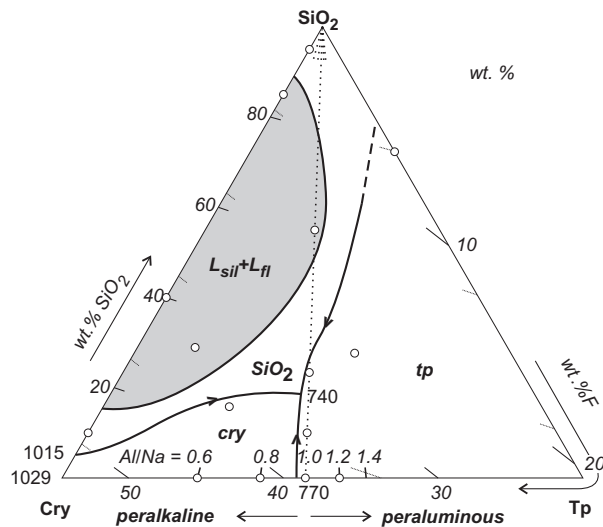


Fig. 14. Liquidus projection of the silica-cryolite-topaz system at 100 MPa. The fluoride-liquid immiscibility extends from the silica-cryolite binary and closes at 960 °C on the quartz liquidus surface. The ternary quartz-cryolite-topaz eutectic is located at 740 °C (30.6 wt % SiO₂, 31.8 wt % F, Al/Na = 0.96). ○, starting compositions. Concentrations of SiO₂, F and variations of the alumina saturation index (Al/Na ratio) are shown on the sides.

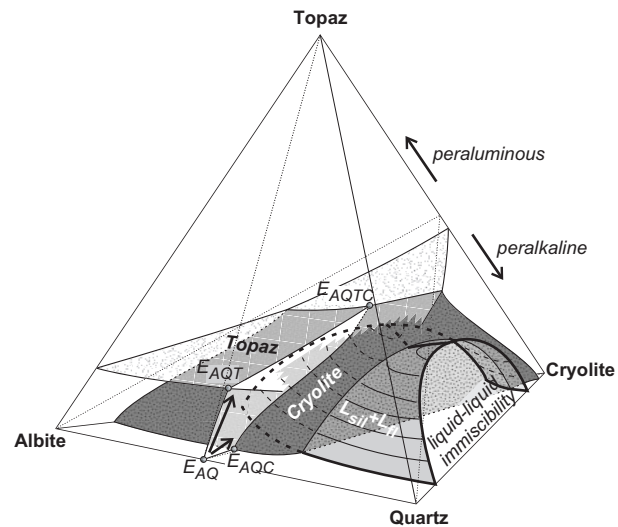


Fig. 16. Schematic liquidus projection of the quaternary quartz-albite-cryolite-topaz system at 100 MPa (wt %). The fluoride-silicate liquid-liquid immiscibility gap is located within the cryolite and quartz volumes. EAQ₂, binary albite-quartz eutectic; EAQTC, ternary albite-quartz-cryolite eutectic; EAQTC, quaternary albite-quartz-topaz-cryolite eutectic. Arrows indicate fractionation paths of peraluminous and peralkaline quartz-albite-precipitating melts, respectively. It should be noted that the quartz-albite cotectic surface does not reach the liquid miscibility gap.

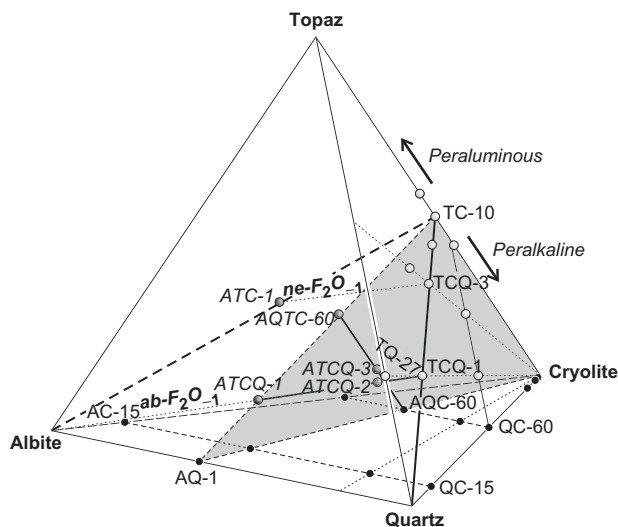


Fig. 15. The quaternary quartz-albite-cryolite-topaz composition space (wt %), with the location of starting compositions and joins. The albite-quartz-TC-10 plane (dashed outline) divides peralkaline from peraluminous composition space. The albite-quartz eutectic, Ab₅₉Qz₄₁ (AQ-1), connects to the topaz-cryolite join along the dotted plane. Filled circles: black, albite-quartz-cryolite ternary (base of the tetrahedron); light gray, quartz-topaz-cryolite ternary (right face); dark gray, quartz-albite-topaz-cryolite quaternary (interior).

GEOLOGICAL IMPLICATIONS

Experimentally determined liquidus relations in the system Na₂O-Al₂O₃-SiO₂-F₂O₋₁ illustrate the location and extent of the silicate-fluoride liquid-liquid

immiscibility and describe liquid lines of descent of natural fluorine-bearing silicic magmas. Addition of fluorine to an albitic composition leads to the quartz-topaz-cryolite ternary, which does not contain any pseudoternary phases. Therefore, this system represents a thermal barrier in the quaternary Na₂O-Al₂O₃-SiO₂-F₂O₋₁ space, and the stability fields of the 'high-fluorination' phases, chiolite and malladrite, are inaccessible to fractionating magmatic systems. We have determined the existence and location of silicate-fluoride liquid-liquid immiscibility in the quaternary silica-albite-cryolite-topaz system. The liquid immiscibility results from coordination differences between individual alkali-aluminofluoride polyhedra and polymerized aluminosilicate framework (Dolejš & Baker, 2005) and it extends from tectosilicate-cryolite binaries towards topaz-bearing systems. In the silica-cryolite binary system, the liquid-liquid miscibility gap is located on the tridymite liquidus above 1100 °C at 0.1–600 MPa. In the albite-cryolite binary system, the two-liquid immiscibility occurs above 1000 °C at 0.1 MPa (Rutlin, 1998) overlying the cryolite liquidus. Within the silica-albite-cryolite ternary, the miscibility gap closes at ~970 °C and its location is inaccessible to crystallization paths of alkali feldspar-saturated peralkaline magmas. Instead, magmatic crystallization will be terminated at the ternary eutectic by crystallization of cryolite at ~770 °C, 100 MPa and ~5 wt % F.

Table 9: *Experimental results in the system silica–albite–cryolite–topaz*

Run	Mix	Pressure (MPa)	Temperature (°C)	Duration (h)	Assemblage	Notes
244	ATCQ-1	100	800	172.6	L + ab (+ qz)	relics of silica
250	ATCQ-1	0.1	750	173.6	L + ab	relics of albite, no equilibrium
243	AQTC-40	100	800	172.6	L	
258	AQTC-40	0.1	720	166.1	L	
242	AQTC-60	100	800	172.6	L	quench microlites
427	AQTC-60	100	750	170.3	L + tp	
275	AQTC-69	100	800	169.5	L + tp	
428	AQTC-69	100	700	174.2	L + tp + cry	
276	ATC-1	0.1	900	167.5	L	
274	ATC-1	100	800	169.5	L	
359	ATCQ-2	0.1	1020	73.8	L	
588	ATCQ-2	100	960	90.8	L	
589	ATCQ-2	0.1	900	117.9	L	
468	ATCQ-2	100	850	145.3	L (+ qz)	no equilibrium
450	ATCQ-2	100	800	164.5	L + qz	no equilibrium
591	ATCQ-3	100	960	90.8	L + cry	
590	ATCQ-3	0.1	900	117.9	L + cry	

Liquid lines of descent of subaluminous and peraluminous silicic magmas are represented by the silica–albite–cryolite–topaz quaternary. The two fluorine-bearing minerals, cryolite and topaz, form a binary eutectic at 770°C, 100 MPa with 39.2 wt % F and cation Al/Na ratio ~0.95. The low temperature of this eutectic causes displacement of other ternary and quaternary eutectics towards this binary join. In the silica–cryolite–topaz ternary, the liquid lines of descent terminate at 740°C, 100 MPa with 31.9 wt % F and cation Al/Na ratio ~0.95. This implies that residual melts in subaluminous systems can evolve to very high fluorine concentrations (in excess of 30 wt %) with a concomitant decrease in SiO₂ (to 30 wt %), without intersecting the fluoride–silicate liquid–liquid immiscibility. In a companion paper (Dolejš & Baker, 2007), we include K₂O and H₂O as additional components and apply experimental results directly to hydrous granitic and rhyolitic systems.

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